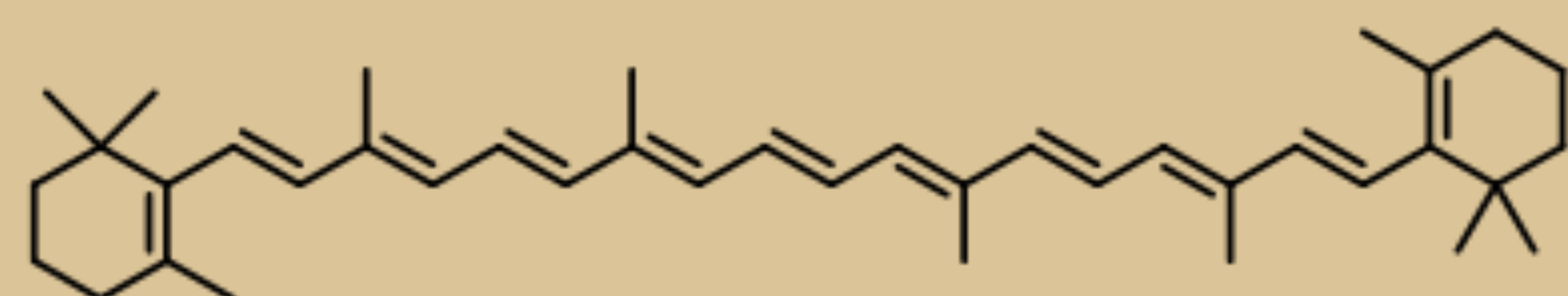


Kinetic Isotope Effects in the Photoisomerization of ^{13}C -Labeled *trans,trans*-1,4-Diphenyl-1,3-Butadiene

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Abstract

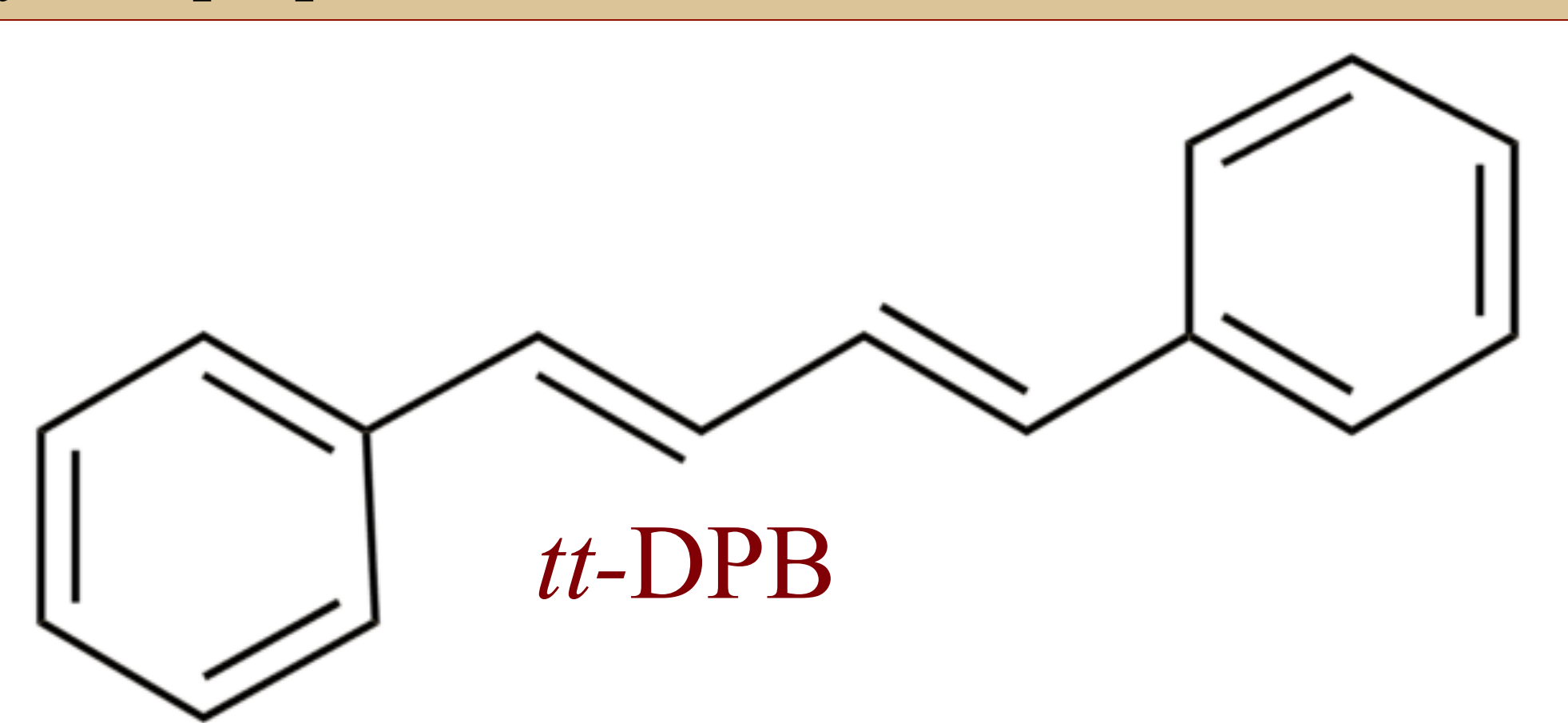
All-*trans*- β -carotene, composed entirely of ^{13}C , undergoes $2A_g$ excited state decay 1.43 times slower than natural β -carotene.¹ Differences in C-C stretching frequencies between excited and ground state account for this result.¹ We wish to determine whether a ^{13}C kinetic isotope effect is also present when the excited state decays primarily via torsional motion. We will carry out a ^1H NMR study of the photoisomerization of *trans,trans*-1,4-diphenyl-1,3-butadiene (*tt*-DPB) labelled with ^{13}C at the 1 position. ^1H NMR analysis of the *cis,trans*-1,4-diphenyl-1,3-butadiene (*ct*-DPB) photoproduct should reveal the relative torsional relaxation rates of the $^{12}\text{C}^{12}\text{C}$ and $^{13}\text{C}^{12}\text{C}$ double bonds. *tt*-DPB- ^{13}C is already on hand.² We plan to compare the photochemical and photophysical properties of *tt*-DPB- ^{13}C to those of natural *tt*-DPB.



β -carotene

Introduction

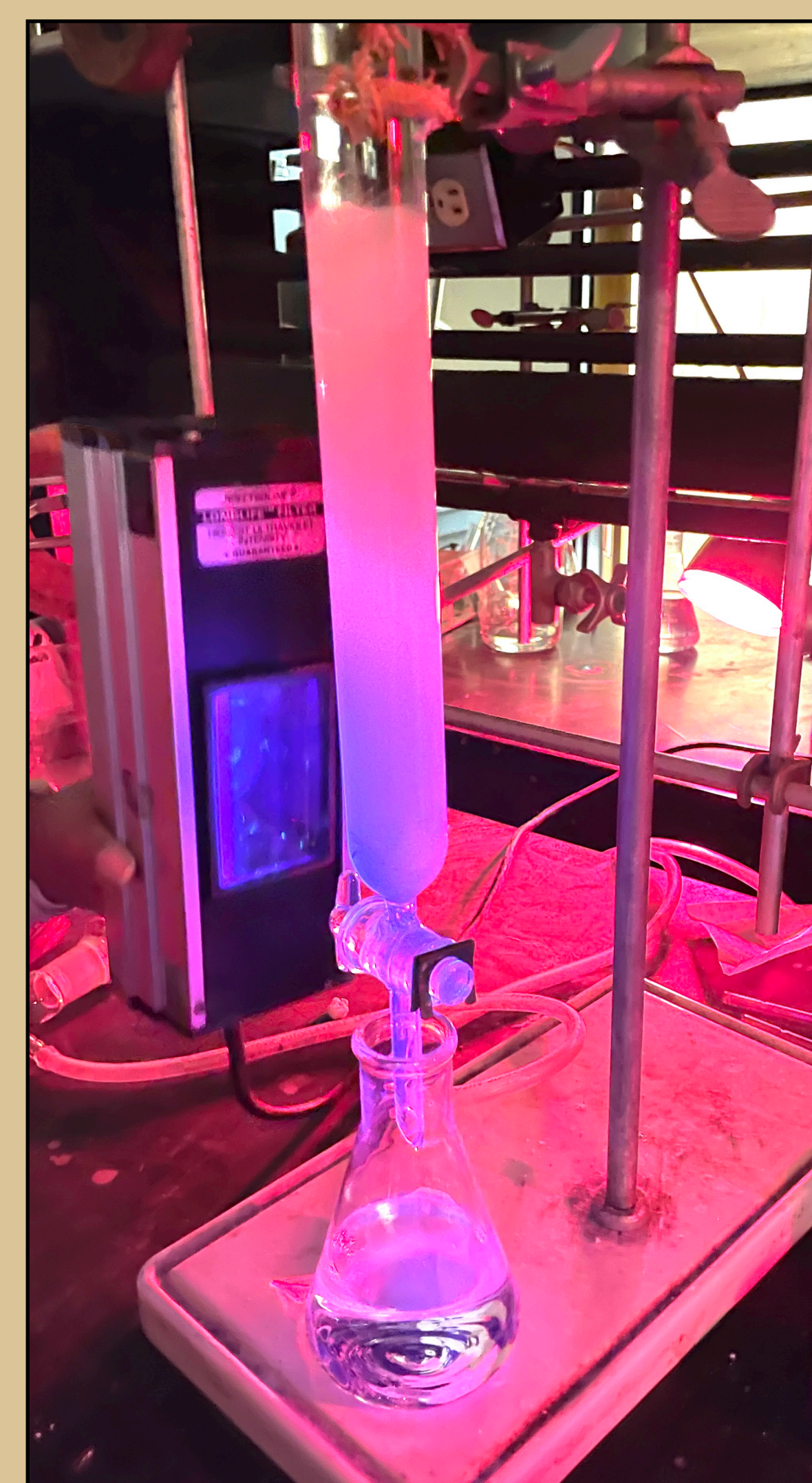
The synthesis of *trans,trans*-1,4-diphenyl-1,3-butadiene-1- ^{13}C (*tt*-DPB- ^{13}C) has been completed.² The next step in our project is to obtain natural abundance C *trans,trans*-1,4-diphenyl-1,3-butadiene (*tt*-DPB) and compare its photochemical and photophysical properties with those of *tt*-DPB- ^{13}C .



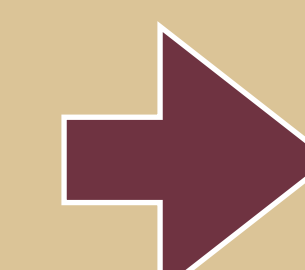
tt-DPB

Methods

We analyzed the initial purity of our ^{12}C -DPB sample using gas chromatography. Our sample was determined to be impure (89%). To purify our compound, we ran a column slurry to separate the sample from its impurities and used a rotavapor to separate the solvent from the compound, making 3 solidified sample fractions. We then used NMR to see which sample fraction was the purest. The process of purifying and analyzing our samples is shown below.



Compound Chromatography

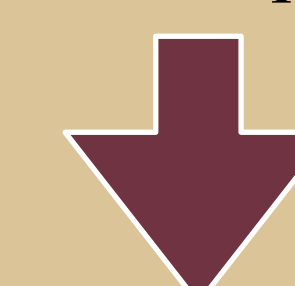


Impurities separated from compound

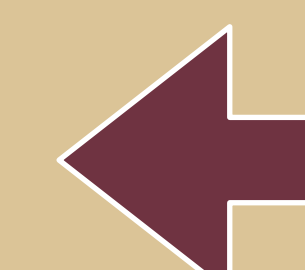


Rotavapor

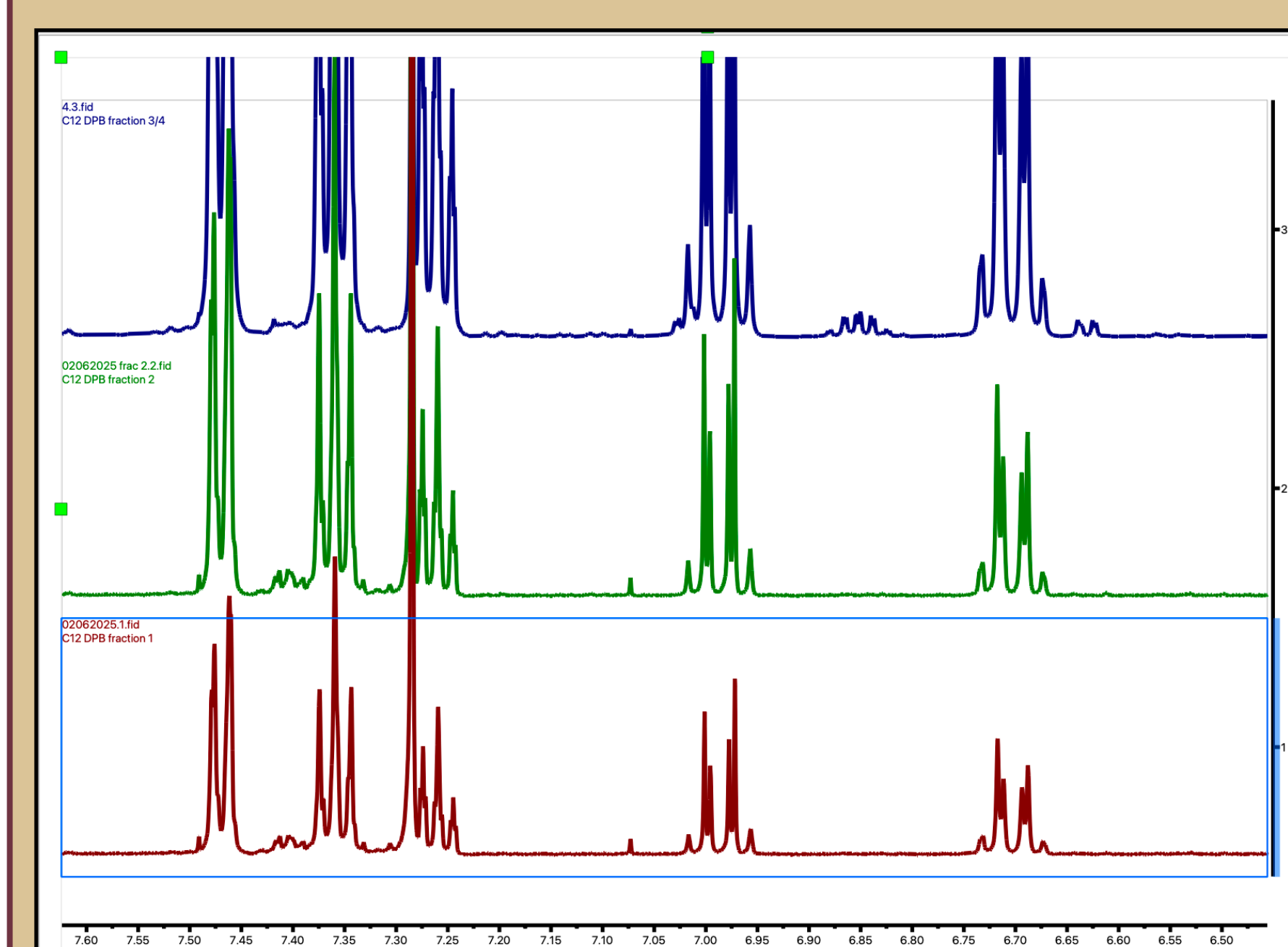
Solvent evaporated from compound



3 sample fractions containing solidified ^{12}C -DPB



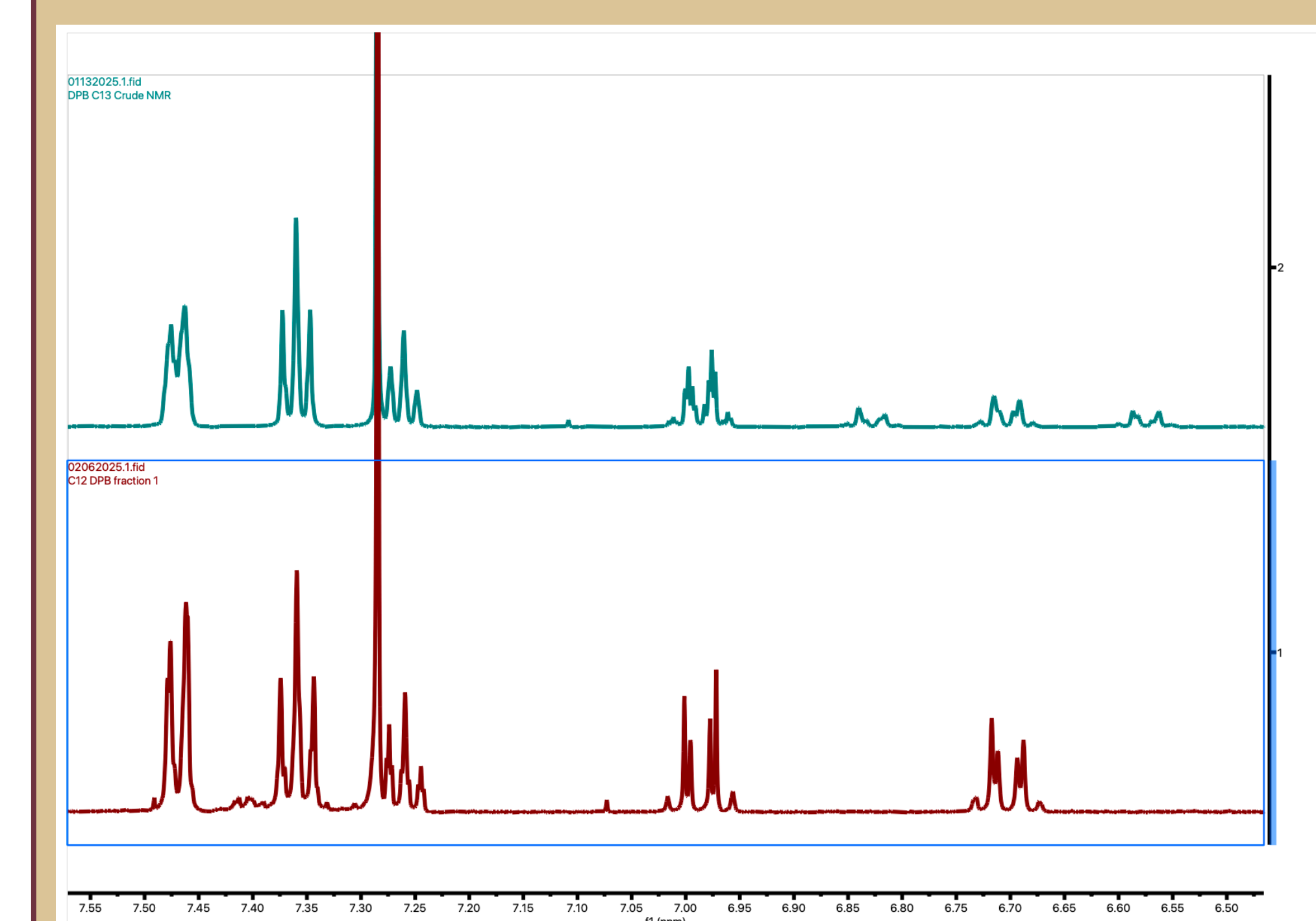
Purity Analyzed



NMR purity Results

Results

Comparing the NMR spectrum of *tt*-DPB- ^{13}C to the known spectrum of *tt*-DPB, we can see that our slurry fraction 1 was our most pure sample.



tt-DPB- ^{13}C NMR (top) vs purest *tt*-DPB NMR (bottom)

Future Work

The next phase of our project includes comparing the photochemistry and photophysics of *tt*-DPB- ^{13}C with those of *tt*-DPB. Of special interest is the determination of the relative efficiency of the photoisomerization of the $^{12}\text{C}^{12}\text{C}$ and $^{13}\text{C}^{12}\text{C}$ double bonds.

References

1. Kuki, M.; Zhang, J.-P.; Sashima, T.; Mukai, I.; Koyama, Y. Vibronic Coupling through the In-Phase, C=C Stretching Mode Plays a Major Role in the $2A_g$ - to $1A_g$ - Internal Conversion of all-*trans*- β -Carotene. *J. Phys. Chem. A* **2000**, *104*, 4155-4166.
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3. Saltiel, J.; Redwood, C. E. Photochemistry of the 1,4-Diphenyl-1,3-butadienes in Ethanol. Trapping Conical Intersections. *J. Phys. Chem. A* **2016**, *120*, 2832-2840.

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